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Statement of Research - The first purpose of this work is to develop a useful model to represent the forces between molecules of moderate complexity containing of the order of five to ten atoms in roughly spherical disposition with the possibility of permanent multipole moments an additionl feature of the systems of interest.

The second aim of this research is to compute the equilibrium and transport properties of these molecules alone and in combination in ranges of density and temperature where measurements are either difficult or unavailable.

A third phase of this work concerns the study of dense fluids.

It will be convenient to discuss each of the objectives separately.

(a) Intermolecular Forces. The spherical shell model for globular molecules has been extended to include the effects a permanent dipole - quadrupole - or octopole - moment on the interaction between pairs of molecules. For molecules where the dipole moment is already known we have computed exactly the first density correction to the equation of state and compared these results to experiment. For the model case of methyl chloride (CH_3Cl) the agreement with experiment was nearly two orders of magnitude over calculations made either with a Lennard-Jones (12-6) model or with a spherical shell model neglecting the dipole moment.

For the interesting molecule, benzene (C_6H_6), our improvement with experiment was well over three orders of

magnitude in a determination which predicts a value of the axial quadrupole moment, Θ_{zz}, of $\pm 15 \times 10^{-26}$ esu. This number is not known experimentally with any certainty, but the estimated values are considerably lower. The size of this moment has encouraged Dr. Patrick Thaddeus of the Institute for Space Studies (NASA) in New York to undertake microwave experiments designed to seek induced absorption in accord with the magnitude of this moment. The experiments have not yet been completed, but we have kept in correspondence on this matter.

For the tetrahedral molecules, CX_4, we have computed the necessary integrals to obtain values of the octopole moments. For the case of methane, CH_4, our value determined from both equilibrium properties and viscosity is in excellent agreement with quantum-mechanical calculations of the same quantity, unlike previous estimates based on other potential functions. For CF_4 we predict a larger value than has been observed, but by a factor nearly the same as the difference between earlier estimates for CH_4 and our results.

In a complementary calculation, we have been able to provide an analytic comparison of this model and the well-known Kihara potential, in which we indicate the principal reasons for the apparent success of the Kihara model in representing polar molecules without including direct provision for them in the model. This result has helped to establish the validity and utility of the spherical shell model.

All of this work has been prepared for publication and of the five papers in question, three have already appeared in

print and are cited below.

(b) Equilibrium Properties. Calculations have been performed of the second and third virial coefficients for spherical shell molecules with permanent moments. For the second virial coefficient, the calculations are given exactly as a series in powers of the reciprocal temperature. For the third virial coefficient, however, only the central part is complete, the integrals needed for the quadrupolar correction are given to terms of the order of θ^4, the higher terms being of much less significance.

A striking outcome of this study is that the corrections to be anticipated for the direct 3-body force are in agreement with the non-additive calculations reported here, but in disagreement with earlier calculations based on a Lennard-Jones model.

All of these computations, as well as those to be discussed next, were supported by NASA grant NsG-398 to the Computer Science Center of the University of Maryland.

(c) Transport Properties. The entire set of transport collision integrals for the spherical shell potential have been computed and employed to exhibit the viscosity of globular molecules. It is known that the effects of a quadrupole moment on the collision integrals is small and we have therefore made no estimate of the multipole expansion upon them. This leads, however, to a direct procedure for estimating octopole moments as follows:

The central parameters of a SS potential are determined from viscosity vs temperature curves. These are then employed to calculate the second virial coefficient. The discrepency noted

is attributed to the octopole moment (provision for other moments, permanent and induced taken into consideration) and a value of the octopole moment selected to fit the virial. It was in this fashion that the excellent agreement for CH_4 reported earlier was obtained. It is a straightforward and useful procedure.

(d) The Cell Model for Clathrates. A convenient approach to the dense fluid has been to constrain a molecule to a cage formed by its neighbors. A successful application of this has been made to the interesting care of a gas hydrate. In earlier studies the common choices for a potential have been the Lennard-Jones or Kihara model. In this work we have utilized the SS potential to probe how well the agreement with experiment can be improved by an improved force law.

Fortunately the improvement is not too large, and we have instead attacked the fundamental problem of improving the theory to include the effects of interactions between adjacent cells. Mr. R. Dorsch - graduate student in physics - has begun this work as part of his Ph.D. thesis.

Publications - The following papers have appeared since January, 1, 1967.

INTERMOLECULAR FORCES IN GLOBULAR MOLECULES. II. MULTIPOLAR GASES WITH A SPHERICAL SHELL CENTRAL POTENTIAL. (with T.S. Storvick and T.H. Spurling) J. Chem. Phys. 46, 599 (1967).

INTERMOLECULAR FORCES IN GLOBULAR MOLECULES. III. A COMPARISON OF THE SPHERICAL SHELL AND KIHARA MODELS. (with T.H. Spurling) Phys. Fluids 10, 231 (1967).

INTERMOLECULAR FORCES IN GLOBULAR MOLECULES. IV. ADDITIVE THIRD VIRIAL COEFFICIENTS AND QUADRUPOLAR CORRECTIONS. (with T.H. Spurling and T.S. Storvick) J. Chem. Phys. 46, 1498 (1967).

In addition papers numbers V and VI have been prepared for submission as follows:

INTERMOLECULAR FORCES IN GLOBULAR MOLECULES. V. TRANSPORT COLLISION INTEGRALS. J. Chem. Phys.

INTERMOLECULAR FORCES IN GLOBULAR MOLECULES. VI. OCTOPOLE MOMENTS OF TETRAHEDRAL MOLECULES. J. Chem. Phys.

Personnel - Professor T.S. Storvick has returned to the University of Missouri following his sabbatical leave spent here. Dr. T.H. Spurling has returned to Australia to begin an appointment at the University of Tasmania, Mr. Robert R. Dorsch is now being supported on this grant.